
CERTAIN NEW DERIVATIVES IN THE AROMATIC
SERIES.

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VI.—*Certain New Derivatives in the Aromatic Series.*

BY HARWOOD HUNTINGTON.

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TABLE OF NEW DERIVATIVES.

- Phenylacridin-azo-alphaNaphtol.
Phenylacridin-azo-betaNaphtoldisulphonic acid, 2 : 6 : 8.
Phenyldimethylacridin-azo-alphaNaphtol.
Phenyldimethylacridin-azo-betaNaphtol.
Phenyldimethylacridin-azo-Naphtylaminesulphonic acid.
Amidoazobenzol-azo-Naphtylaminesulphonic acid, 2 : 7.
Para-Anisidin-azo-alphaNaphtoldisulphonic acid, 1 : 4 : 8.
Para-Anisidin-azo-betaNaphtylaminesulphonic acid, 2 : 5.
Para-Anisidin-azo-betaNaphtol.
Fluoren-disazo-betaNaphtylamine.
Fluoren-disazo-beta-gammaNaphtylamine.
Fluoren-disazo-alphaNaphtolsulphonic acid, 1 : 4.
Fluoren-disazo-betaNaphtolsulphonic acid, 2 : 6.
Fluoren-disazo-alphaNaphtol.
Fluoren-disazo-betaNaphtol.
Tetramethyldiamidodiphenylmethan-azo-betaNaphtylaminesulphonic acid, 2 : 5.
Tetramethyldiamidodiphenylmethan-azo-betaNaphtylaminesulphonic acid, 2 : 6.
Tetramethyldiamidodiphenylmethan-azo-betaNaphtylaminesulphonic acid, 2 : 7.
Tetramethyldiamidodiphenylmethan-azo-beta-gamma-Naphtylaminesulphonic acid, 2-3.
Tetramethyldiamidodiphenylmethan-azo-alphaNaphtol.
Tetramethyldiamidodiphenylmethan-azo-alphaNaphtol sulphonic acid, 1 : 4.
Tetramethyldiamidodiphenylmethan-azo-betaNaphtol sulphonic acid, 2 : 6.
Tetramethyldiamidodiphenylmethan-azo-betaNaphtoldisulphonic acid, 2 : 6 : 8.
Tetramethyldiamidodiphenylmethan-azo-betaNaphtoldisulphonic acid, 2 : 3 : 6.
Aniline-azo-dialphaNaphtol.
Aniline-azo-dibetaNaphtol.

Para-Nitraniline-azo-dialphaNaphtol.
 Para-Nitraniline-azo-dibetaNaphtol.
 Toluidine-azo-dialphaNaphtol.
 Toluidine-azo-dibetaNaphtol.
 Xylidine-azo-dialphaNaphtol.
 Xylidine-azo-dibetaNaphtol.
 Amidoazobenzol-azo-dialphaNaphtol.
 Amidoazobenzol-azo-dibetaNaphtol.
 Sulphanilicacid-azo-alphadiNaphtol. •
 Sulphanilicacid-azo-betadiNaphtol.
 AlphaNaphtylamine-azo-alphadiNaphtol.
 Naphthionicacid-azo-alphadiNaphtol.
 Naphthionicacid-azo-betadiNaphtol.
 BetaNaphtylaminesulphonicacid-azo-alphadiNaphtol.
 BetaNaphtylaminesulphonicacid-azo-betadiNaphtol.
 Chinolin-azo-betaNaphtylaminesulphonic acid, 2 : 5.
 Chinolin-azo-alphaNaphtolsulphonic acid, 1 : 4.
 Chinolin-azo-beta-gammaNaphtylaminesulphonic acid.
 betaNaphtylaminesulphonic acid (2 : 6)-azo-alphaNaphtoldisulphonic acid, 1 : 4 : 8.
 betaNaphtylaminesulphonic acid (2 : 5)-azo-betaNaphtol.
 betaNaphtylaminesulphonic acid (2 : 5)-azo-betaNaphtoldisulphonic acid, 2 : 6 : 8.
 betaNaphtylaminesulphonic acid (2 : 5)-azo-betaNaphtoldisulphonic acid, 2 : 4 : 8.
 betaNaphtylaminesulphonic acid (2 : 5)-azo-alphaNaphtoldisulphonic acid, 1 : 4 : 8.
 Naphthionic acid-azo-alphaNaphtoldisulphonic acid, 1 : 4 : 8.
 Tribromaniline-azo-betaNaphtol.
 Metadioxyazotribrombenzol.
 Tribromaniline-azo-alphaNaphtolmonosulphonic acid, 1 : 4.
 Tribromaniline-azo-betaNaphtolmonosulphonic acid, 2 : 6.
 Tribromaniline-azo-betaNaphtoldisulphonic acid, 2 : 3 : 6.
 Tribromaniline-azo-alphaNaphtoldisulphonic acid, 2 : 6 : 8.
 Tribromaniline-azo-alphaNaphtylamine.
 Tribromaniline-azo-betaNaphtylamine.
 Tribromaniline-azo-betaNaphtylaminesulphonic acid, 2 : 5.
 Tribromaniline-azo-betaNaphtylaminesulphonic acid, 2 : 6.

PREFACE.

It is a wide-spread, popular idea that the Coal-Tar Industry has revolutionized the theory and practice of dyeing. This is only true in part, because the improvement made possible by the brilliant work of the leaders in Color-Chemistry has been in great measure annulled by the dyers, who, instead of using the best and most

reliable of the inventions, have fallen into the reprehensible habit of using those many fugitive derivatives of aniline with which the market is flooded, because they are a little cheaper. All the colors of the spectrum can now be made from the Coal-Tar Colors, and it is perfectly possible to make them thoroughly reliable and fast—fast to washing with hot and cold water, fast to acidulated water, or alkaline water, and what is perhaps the supreme test of a color, fast to the action of sunlight. If the dyers would conscientiously use the really good dyes from coal-tar, and avoid the worthless ones with which their trade is infested, the civilized part of the world could compete successfully with those dyes used by the makers of the Persian and Turkish carpets, in which the colors are as durable as the rugs themselves.

To-day it is a fact, that, in spite of the many valuable and reliable dyes, many of the old-fashioned dyes are not driven out of the market. The natural dyes are still used in immense quantities—Indigo for blue, Logwood for slates and blacks, Cutch for browns, Fustic for yellows, and Sumac for mode colors. Then there are the ancient uses of iron nitrate to make buffs with alkalies; the Prussian blues from iron nitrate and prussiate; the brown from manganese and alkalies; and the yellow from lead acetate and bichromate; all these are of daily application. In many cases it is a pity, and in most instances it is a sad waste of more or less expensive chemicals, but as yet, only in the case of cochineal and madder is the field completely occupied by the artificial dyes.

The writer cannot refrain from making one more observation here. It is that the methods of dyeing are sure to undergo a modification in the near future. Many dyes which now are made for the works at the aniline mill or factory, will be made at the works where the colors are applied to the fabric. As the patents run out the number of colors available for manufacture at the works will increase, and skilled color chemists will be as much a requisite in works of repute, as the now omnipresent and sometimes omniscient Superintendent. This is not necessarily a factor which will act to the detriment of the aniline manufactories, for there will always be a demand for aniline dyes in the dry state; the advantages of, and the necessities for the division of labor are too apparent to be gainsaid; but in large works there is a deal of saving and small economies to be effected, and the most progressive and enterprising establishments are sure to be the first to profit by the

intelligent, conscientious work of able and competent chemists of the new school.

In lieu of an historical introduction, I have drawn up a list of all the important dyes now prepared from coal-tar, and have indicated their modes of manufacture. This table forms no part of my thesis proper, which is strictly original work, but is offered to show the present status of the color industry, and to give its salient points. The list by no means comprises the whole number of dyes which have been made, but simply gives the principal ones, and those which have obtained a permanent place in the commercial world; and after all, that is a fair test of the usefulness and intrinsic value of any product.

NITRO DYES. Type, $R.NO_2$.

Naphtol Yellow. HNO_3 on α -Naphtoltrisulphonic acid, 1 : 2 : 4 : 7.

AZOXY DYES. Type, $\begin{array}{c} R.N \\ | \\ R.N \end{array} \rangle O$

Curcumine. p -Nitrotoluolsulphonic acid and KOH.

HYDRAZONE DYES. Type, $R-NH-NH-R$.

Tartrazine. Phenylhydrazinemonosulphonic acid and dioxytartaric acid.

AZO DYES. Type, $R.N=N.R$.

Cochineal Scarlet G. Aniline and alphanaphtolsulphonic acid C, 1 : 5.

Ponceau 4GB. Aniline and betanaphtolsulphonic acid, Schæffer's, 2 : 6.

Orange G. Aniline and betanaphtoldisulphonic acid, "G", 2 : 6 : 8.

Chrysoidine. Aniline and phenylenediamine.

Wool Scarlet R. Xylidine and alphanaphtoldisulphonic acid, Schœllkopf's, 1 : 4 : 8.

Palatine Scarlet. Metaxylidine and naphtoldisulphonic acid.

Erika B. Dehydrothiometaxylidine and alphanaphtoldisulphonic acid.

Fast Red A. Naphthionic acid, 1 : 4, and betanaphtol.

Azo-Rubine S. Naphthionic acid and alphanaphtolsulphonic acid, Neville and Winther's, 1 : 4.

Fast Red E. Naphthionic acid and betanaphtolsulphonic acid, Schæffer's, 2 : 6.

New Coccine. Naphthionic acid and betanaphtoldisulphonic acid, "G", 2 : 6 : 8.

Fast Red D. Naphthionic acid and betanaphtoldisulphonic acid, "R", 2 : 3 : 6.

Ponceau 6R. Naphthionic acid and betanaphtoltrisulphonic acid.

Azo-Coccine 7B. Amidoazobenzene and alphanaphtolsulphonic acid, Neville and Winther's, 1 : 4.

Brilliant Croceine. Amidoazobenzene and naphtholdisulphonic acid, "G", 2 : 6 : 8.

Croceine 3B. Amidoazotoluol and naphtholdisulphonic acid, Schœllkopf's, 1 : 4 : 8.

Double Scarlet. Amidoazobenzolsulphonic acid and betanaphtol.

Biebricher Scarlet. Amidoazobenzoldisulphonic acid and betanaphtol.

Ponceau S extra. Amidoazobenzoldisulphonic acid and betanaphtoldisulphonic acid, "R", 2 : 3 : 6.

Croceine Scarlet 7B. Amidoazotoluolsulphonic acid and betanaphtolsulphonic acid, Bayer's, 2 : 6.

Bordeau G. Amidoazotoluolsulphonic acid and betanaphtolsulphonic acid, Schæffer's, 2 : 6.

Jet Black R. Amidobenzoldisulphonic-acid-azoalphanaphtylamine and phenylalphanaphtylamine.

Naphtol Black 6B. Alphanaphtylaminedisulphonic-acid-azonaphtylamine and betanaphtoldisulphonic acid, "R", 2 : 3 : 6.

St. Denis Red. Diamidoazoxytoluol and alphanaphtolsulphonic acid, Neville and Winther's, 1 : 4.

Chrysophenine. Ethyliring Brilliant Yellow.

Cresotine Yellow. Benzidine and cresotinic acid.

Chrysamine G. Benzidine and salicylic acid.

Diamine Black R. Benzidine and amidonaphtolsulphonic acid.

Sulfon-Azurine. Benzidinsulfondisulphonic acid and phenylbetanaphtylamine.

Delta-purpurine 5B. Tolidine and naphtylaminisulphonic acid.

Brilliant Congo R. Tolidine and naphtylaminisulphonic acids, "R", 2 : 3 : 6, and Bronner's, 2 : 6.

Toluylene Orange R. Tolidine and toluylenediaminesulphonic acid.

Rosazurine G. Tolidine and methylbetanaphtylaminesulphonic acid.

Benzoazurine G. Dianisidine and alphanaphtolsulphonic acid, Neville and Winther's, 1 : 4.

Benzopurpurine 10B. Dianisidine and naphthionic acid.

OXYKETONE DYES.

Alizarine Black S. From dinitronaphtaline.

Alizarine No. 1. From anthrachinonemonosulphonic acid.

Alizarine SDG. From anthrachinonedisulphonic acid.

Alizarine RX. From beta-anthrachinonedisulphonic acid.

Alizarine Orange. HNO_3 on alizarine.

Alizarine Powder 5 WS. H_2SO_4 on alizarine.

Alizarine Blue. Glycerine and H_2SO_4 on betanitroalizarine.

DI-PHENYL-METHANE DYES.

Auramine O. Tetramethyldiamidobenzophenone and AmCl and ZnCl_2 .

TRI-PHENYL-METHANE DYES.

Malachite Green. Benzaldehyde and dimethylaniline.

Brilliant Green. Benzaldehyde and diethylaniline.

Magenta. Aniline and toluidine.

Methyl Violet. Dimethylaniline.

Hofmann's Violet. Action of methyl halogens on Magenta.

Methyl or Cotton Blues. Sulfurizing Triphenyl-p-Rosaniline.

Alkali or Nicholson's Blue. Sulfurizing Aniline Blue.

Fluoresceine, or Uranine. Phthalic acid anhydride and resorcin

Eosines. Bromiring Fluoresceine.

Erythrosine. Iodiring Fluoresceine.

Phloxine. Bromine on tetra-chlor-fluoresceine.

Rose Bengale. Iodine on tetra-chlor-fluoresceine.

Galleine. Phthalic acid anhydride and gallic acid.

Coerulein. Galleine and H_2SO_4 .

INDOPHENOLS.

Indophenol. Nitrosodimethylaniline and alpha-naphtol.

OXAZINE AND THIAZINE DYES.

Gallocyanine. Nitrosodimethylaniline and gallic or tannic acid.

Fast Black. Nitrosodimethylaniline and m-oxydiphenylamine.

Methylene Blue. From p-Amidodimethylaniline and dimethylaniline.

Toluidine Blue. From p-Amidodimethylaniline and o-toluidine.

SAFRANINES.

Safranine. Oxidation of p-Toluylendiamine, Aniline and o-Toluidine.

INDULINES AND NIGROSINES.

Nigrosine. Action of H_2SO_4 on Indulines; latter from amidoazobenzene heated with aniline.

Paraphenyleneblue R. Phenylendiamine on amidoazobenzene.

ARTIFICIAL INDIGO.

Indigo Salt. Bisulfite compound of o-nitro-phenyl-lactic acid methyl-ketone.

CHINOLINE DYES.

Chinolin Yellow. Chinaldin and phthalic acid anhydride.

ACRIDINE DYES.

Phosphine. Bye-product in manufacture of Magenta.

THIO-BENZYL DYES.

Primuline. p-toluidine heated with S., and sulfuring the product.

DYES OF UNKNOWN CONSTITUTION.

New Gray. Boiling nitrosodimethylaniline with H_2O or C_2H_5OH .

Aniline Black. Oxidation of aniline with chlorates, chromates or copper salts.

Cachou de Laval. Fusing organic substances, as starch, bran, etc., with Na_2S .

Hemolin. Action of NaNO_2 on logwood.

This list covers the whole territory of the Coal-Tar Colors, and gives representatives of every class of artificial dyes. I now pass to the original work. It is a pleasure and a privilege to express obligations and gratitude to Professors Charles F. Chandler and Charles E. Colby for their kind encouragement and many favors extended while this thesis was in the process of construction. The creditors have been well chosen by their debtor, who only becomes one of a large number.

THE PROPOSITIONS which this thesis undertakes to establish are:—

- I. That Fluoren is capable of giving derivatives which will compare with the dyes from benzidine, tolidine, and dianisidine.
- II. That Leuk-Auramine can be used to give very resistant colors.
- III. That Di-Naphtols increase the strength of dyes as they heighten the molecular weight.
- IV. That Chinoline will give reliable colors.
- V. That Schœllkopf's Acid, 1 : 4 : 8, gives, as a rule, colors which are fast to light.
- VI. That Bromine is disadvantageous in the Azo-Group.

The work described in the following pages was undertaken in the hope of making new derivatives of coal-tar which would rival the dyes already in commerce. Many now in common use in the practical world give colors which are fast in some respects, and not easily to be surpassed in their special qualifications. But there are no dyes which combine all the desirable qualities. To be perfect a dye must be able to withstand prolonged exposure in the sunlight, and further, resist washing with all the ordinary household chemicals.

To give an idea of the state of the field in which the work of this thesis was done, a brief statement of the best three starting-points for azo dyes is given here.

$$\begin{array}{c} \text{C}_6\text{H}_4.\text{NH}_2 \\ | \\ \text{C}_6\text{H}_4.\text{NH}_2 \end{array}$$

a. Benzidine, is used for yellows, blacks, and reds in the cases of the dyes—

Chrysamine G., made with benzidine and salicylic acid.

Diamine Black, benzidine and amido-naphtol-sulphonic acid.

Diamine Fast Red, made from benzidine and amidonaphtolsulphonic acid with salicylic acid.

Diamine Red NO, manufactured from ethoxybenzidine and naphthylamine sulphonic acid.

Diamine Blue 3R, from ethoxybenzidine and alphaNaphtol-sulphonic acid.

b. Tolidine, $\begin{array}{c} \text{C}_6\text{H}_3\cdot\text{CH}_3\cdot\text{NH}_2 \\ | \\ \text{C}_6\text{H}_3\cdot\text{CH}_3\cdot\text{NH}_2 \end{array}$ is used for a number of good colors—reds; yellows, oranges, and pinks.

Benzopurpurine 4B, made from diazotized tolidine and naphthionic acid.

Benzopurpurine B, from tolidine and naphthylamine-sulphonic acid, 2 : 6.

Chrysamine R, from benzidine and salicylic acid.

Toluylene Orange, from tolidine and toluylendiaminsulphonic acid.

Rosazurine B, from tolidine and methyl-naphthylamine-sulphonic acid.

c. And there are a number of dyes, blues and reds, made from dianisidine, which hold a firm place in the commercial world. Dianisidine is,

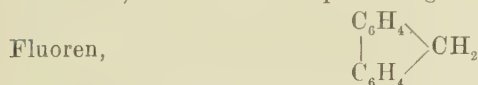


Benzoazurine G, where the dianisidine is diazotized and coupled with naphtolsulphonic acid, 1 : 4.

Benzopurpurine 10B, dianisidine and naphthionic acid, 1 : 4.

From an observation of the constitution of the benzidine, tolidine, and dianisidine, it becomes evident that the chemicals which give the best results must have, first, the amido group; second, as much the polycyclical construction as possible; and thirdly, should have the highest possible molecular weight.

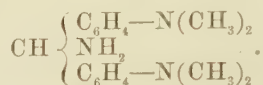
I. The first chemical which was taken up in the course of these researches, as a chemical possessing the desired properties, was



As had been foreseen, fluoren gave several very interesting dyes, all of which had the properties most sought for in good colors—

brightness and stability. The results are given in detail in Part Second of the thesis.

II. Another hold on the subject was suggested to the writer on noticing the composition of leuk-Auramine,



That this compound was diazotizable was readily seen; and that if it would link with the naphthols, naphtylamines, and their sulphonic acids, it would give dyes with the unique characteristic of being the first dye which had been made where the diphenyl-methane group was linked with naphthols. Success was attained in the coupling, and colors were made which possessed many desirable properties. The detailed work of the experiments are given in the technical part of the thesis.

III. For increasing the complexity of the molecule, it was determined to use dinaphthols in lieu of the ordinary naphthols; this increased the molecular weight of the dyes made, and although it is early to predict marked success, it is to be said that the colors dyed from the dinaphthols are resisting the action of light to a remarkable degree.

IV. Chinoline offered another chemical as a proper subject for investigation, as it had a polycyclical formation, was of considerable molecular weight, and amido groups could be put into the molecule.



When changed to a nitro derivative, and then reduced to the amido form, and subsequently diazotized and coupled with naphthol or naphtylamine, sulphonic acids, several new compounds with the desired characteristics were obtained.

V. It had long been noticed by the writer that the Schœllkopf's acid, $\text{C}_{10}\text{H}_5\text{OH}(\text{SO}_3\text{H})_3$, 1 : 4 : 8, gave staunch azo dyes. Those which are already commercial articles are—

Wool Scarlet R, where xyloidine is diazotized and linked with the Schœllkopf's acid.

Croceine 3B, which uses amido-azo-toluol.

Bordeau G, in which instance amidoazotoluolmonosulphonic acid is used.

In part II of this thesis three new dyes are described which have been made from the Schœllkopf's acid by different amido derivatives.

VI. In proving that bromine was not advantageous, the work simply resolved itself to the making of a series of well-known dyes, and then making dyes of precisely similar character, starting with chemicals into which bromine had been introduced. Three atoms of bromine were used in all the cases. The results show that bromine throws the hue of a dye toward the orange in the case of the azo dyes. In the case of eosines, bromine is essential to the formation of the color; here it turns the shade away from the desired clear red. The manner in which the work was done is shown in the practical work of the thesis.

A considerable number of other researches were made in the course of the year, and some of them gave very interesting results, and will lead to further work. But it has been decided not to incorporate them in this thesis, as the main points which the thesis attempts to prove are decided by the results obtained in the work already outlined, and given in detail in the latter part of the work. It may be as well to mention some on this additional work; chrys-aniline when diazotized and linked with alphanaphtol gave a dark purple (sample No. 9), and when coupled with the "G" salt, beta-naphtol-disulphonic acid, 2 : 6 : 8, a bright red dye (sample No. 10).

Chrysaniline is,



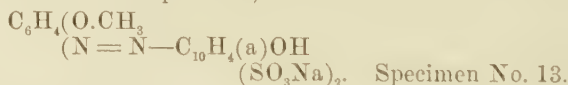
Benzoflavine, the isomer of Chrysaniline, gave results which were not uninteresting. With alpha-naphtol it gave a crimson (sample

No. 11); with beta-naphtol also a crimson (sample No. 12). Naphthylamine-sulphonic acids generally gave reds. Benzoflavine is—



Amidoazobenzene has been studied a great deal, but the writer has been able to get new derivatives from it. The dyes now known are Sudan III; Azo-Coccine 7B; Crocein B; Brilliant Crocein; Ponceau SS; and Ponceau 5R. The author diazotized in the usual manner, and made four different browns or drabs, and one red, the last being made with the union of the diazotized amidoazobenzene with the Bayer's acid, 2 : 7, and it was found to have the formula, $\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}=\text{N}-\text{C}_{10}\text{H}_5(\text{SO}_3\text{Na})\cdot\text{NH}_2$.

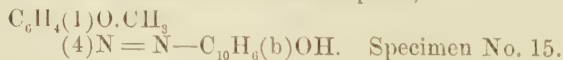
Ortho-Anisidine, $\text{C}_6\text{H}_4(1)\text{O}\cdot\text{CH}_3\cdot(2)\text{NH}_2$, has been used since 1878, when it was applied in the formation of Anisol Red, sometimes called Anisidine Ponceau. Azo Eosine is another derivative from the ortho-anisidine. But para-Anisidine seems not to have been used. Three new dyes were made, one a pink, by the application of Schœllkopf's acid,



The second an orange with Dahl's acid,



The third a Bordeaux with beta-naphtol,

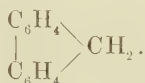


PART II.

PRACTICAL WORK ON THE NEW DERIVATIVES.

I. The use of the three compounds, benzidine, tolidine, and anisidine, suggested the thought, that if other compounds of similar character—that is, bearing amido groups, possessing if possible a polycyclical structure, and of high molecular weight—were to be applied, perhaps dyes would result which would be as good or better.

Fluoren, therefore, was taken in hand. It has the formula,

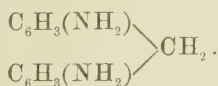


Fluoren has never been developed, probably on account of its high price. But in the coal-tar industry, the price of a chemical is never an obstacle which stands in the way of its application in a color for a very long time, as means are eventually found for the more economical manufacture of the desired compound. As, for instance, the alizarine industry, where the anthrachinone was only a chemical curio in museums until its presence in enormous quantities was wanted, when it became as reasonable in cost as could be expected.

Fluoren, or diphenyl-methane, is found in coal-tar, and can be synthesised by passing diphenyl through hot tubes; or by the distillation of diphenyl-ketone with zinc dust; or treating diphenyl-ketone with phosphorous and hydriodic acid; and also by distillation of phenanthrachinone with lime.

Fluoren is changed to dinitro-fluoren by adding it to a mixture of equal parts of nitric and glacial acetic acids. The fluoren which was unconverted was separated from the dinitrofluoren by washing with hot alcohol; then it was crystallized from glacial acetic acid. Fluoren has a melting-point of 112; the dinitro-derivative melts at 199–201.

This dinitro-fluoren was changed to the diamido derivative by the addition of tin to the acid solution. The formula of the diamido fluoren is,



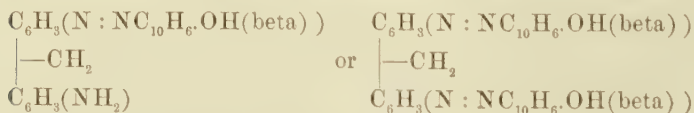
On diazotizing two kilos of this with seven hundred grammes of sodic nitrite and twelve hundred grammes of hydrochloric acid of twenty Baumé, the diazotized compound will link with different naphthols, naphthylamines, and their sulphonic acids, to give the results herewith appended.

beta-Naphtylamine,	Brown.
beta and gamma naphthylamine,	Red, Sample No. 6.
Neville and Winther's, Naphtol-sulphonic, 1 : 4,	Red.
Schæffer's acid, naphtol-sulphonic, 2 : 6, . .	Purple.
alpha-Naphtol,	Orange, Sample No. 7.
beta-Naphtol,	Rose, Sample No. 8.

The reaction is facilitated by stirring, and by heating the liquid to about 80 degrees Centigrade. The dye is precipitated by the addition of sodic acetate and common salt; then it is pressed, dried, and analysed.

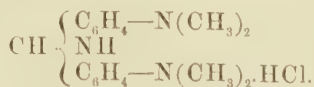
The dyes produced by the union of the diazotized diamido-fluoren and the different naphthylamine sulphonic acids, are all reds, soluble easily in water with a yellowish-red coloration; with hydrochloric acid they turn to a pink, if the acid is fully concentrated; with concentrated sulphuric acid the dyes dissolve, and give a violet similar in hue to the Hofmann's violet; with alkalies a yellow precipitate is produced.

It was desired to find out whether the diazotization effected both the amido groups, or only one. Whether the formula of the new coloring matter, in the case, for instance, of beta-Naphtol, was



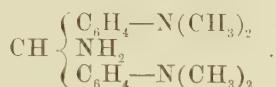
Analysis showed that both amido groups were diazotized and were linked

II. The second line of work was begun with the diphenyl-methane compound, Auramine, which has the formula,

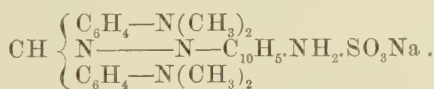


Auramine O should be used, for Auramine I or II is not pure.

This can be reduced by the action of sodium-amalgam, or indeed any reducing agent, to the form of Leuk-Auramine,



If three kilos of the Auramine has been taken in the beginning of the operations, seven hundred grammes of sodic nitrite should be employed in the diazotization, with twelve hundred grammes of hydrochloric acid of twenty Baumé. The reaction is complete in the course of half an hour, when the coupling is proceeded with. It should be noted that it is not necessary in this reaction to isolate the diamido product in the dry or solid state; the coupling with the desired naphtol can be effected just as well in the same solution where the reduction has taken place. In the instance of naphtylamine-sulphonic acid, 3.22 kilos are taken. Coupling is facilitated by stirring and by heating the liquid to about eighty degrees Centigrade. The dye is precipitated by the addition of sodic acetate and common salt. Then it is filtered out, pressed, dried, and analysed. In the case of naphtylamine-sulphonic acid, the dye is proved to have the constitution,



Other compounds can be linked, as is shown in the table which is appended.

Naphtylamine-sulphonic acid, Bronner's, 2 : 6,	Red.
Naphtylamine-sulphonic acid, Dahl's, 2 : 5,	Red, Sample No. 22.
Naphtylamine-sulphonic acid, Bayer's, 2 : 7,	Brown.
Naphtylamine-sulphonic acid, mixture of	
2 and 5,	Red, Sample No. 23.
alpha-Naphtol,	Orange.
Naphtol-sulphonic acid, N. and W., 1 : 4,	Rose.
Naphtol-sulphonic acid, Schæffer's, 2 : 6,	Brown.
Naphtol-disulphonic acid, 2 : 6 : 8, "G",	Orange, bright.
Naphtol-disulphonic acid, 2 : 3 : 6, "R",	Orange, dull.

III. The third line of working, employed in the thesis commenced with the naphtols, and employed the di-naphtols, as they have a higher molecular weight.

The naphtols, both alpha and beta, are used in the manufacture

of many dyes, and the most important can be so readily seen in the table given below, that they are not further specified here.

Di-naphtols are made by heating naphtols with water, and then cooling; then the liquid is filtered, and to the filtrate ferric chloride is added until the violet color will not increase in intensity. Filter, dry, and recrystallize.

The reaction runs in accordance with the following equation,



	a-Naphtol.	a-di-Naphtol.	b-Naphtol.	b-di-Naphtol.
Aniline,	New red,	Black-violet,	<i>Sudan I</i> ,	Orange.
p-Nitraniline,	Rose,	Violet,	<i>Ingrain red</i> ,	. . .
p-Toluidine,	Bordeau,	Rose,	Brick red,	Yellow.
Xylidine,	Black-brown,	Bordeau, No. 24,	<i>Sudan II</i> ,	Orange.
Amidoazobenzol,	Black-violet,	Violet,	<i>Sudan III</i> ,	Rose.
Sulphanilic,	<i>Naphtol orange</i> ,	Good red,		Red.
a-Naphtylamine,	<i>Sudan brown</i> ,	Black,		. . .
b-Naphtylamine,			<i>Carmin naphtha</i> ,	. . .
Napthionic,	<i>Naphtylam. brown</i> ,	Violet-black,	<i>Fast red A</i> ,	Brown-red,
		No. 25,		No. 26.
Bronner's,	<i>Fast brown 3B</i> ,	Red,	<i>Double brilliant</i>	Rose.
			<i>Scarlet</i> ,	

Italicized names are old dyes.

IV. *Chinoline*, with its bi-cyclical constitution, gave a suggestion for another line of work which it was hoped would terminate successfully.



Chinoline is found in coal-tar, and is also made artificially by heating in a return condenser a mixture of nitrobenzene, aniline, glycerine, and sulphuric acid.

The manner of working with the chinoline was as follows: First, it was nitrated by allowing a solution of chinoline in nitric acid to run into a mixture of nitric and sulphuric acids; this nitrochinoline was reduced to the amido-chinoline, and the amido compound diazotized in the usual way, and then coupled with sulphonic acid salts of naphtylamines and naphtols. The most interesting results were the following:—

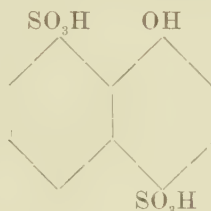
When coupled with equal molecules of Dahl's acid, naphtylamine-sulphonic acid, 2 : 5, a red dye was produced. Specimen is annexed, labelled No. 16.

When combined with Neville and Winther's acid, naphtol-sulphonic acid, 1 : 4, a crimson dye was made. Specimen No. 17.

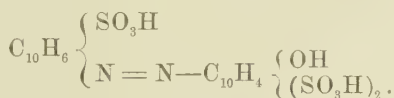
When coupled with the technical mixture of beta and gamma naphtylaminesulphonic acids, a brown-red was produced. Specimen No. 18.

All the dyes, No. 16, No. 17, No. 18, are precipitated by the addition of common salt, then filtered out and dried.

V. The fact that Schœllkopf's acid, alphaNaphtoldisulphonic acid, 1 : 4 : 8, gave nearly, if not quite, the fastest of the colors



of the Azo Group, was proved by a series of experiments for other dyes. Bronner's acid, or naphtylamine-sulphonic acid, 2 : 6, was worked upon for new derivatives, and although it has been used with a-Naphtol for Fast Brown 3B; and with beta-Naphtol for Double Brilliant Scarlet; and with Neville and Winther's acid, naphtol-sulphonic acid, 1 : 4, for Double Scarlet Extra; yet it was found that other combinations were feasible, and that among half a dozen other new derivatives, the best was that obtained when the Schœllkopf's was used. There a red was given which was very fast to the action of sunlight. Analysis proves the constitution to be—



	Theory.	Found.
Carbon, . . .	44.6 per cent	44.4 per cent.
Hydrogen, . . .	2.6 "	2.9 "
Oxygen, . . .	29.7 "	29.4 "
Nitrogen, . . .	5.2 "	5.5 "

Of course, the dye when used is used in the form of its sodium salt. The specimen attached is numbered No. 1.

The next step in the research was the examination of Dahl's acid, betanaphthylamine-sulphonic acid, $C_{10}H_6NH_2(2)SO_3H(5)$. Dahl's is already used for some of the dyes in commerce at the present time. One of these is made by the linking of the diazotized Dahl's acid with Neville and Winther's acid, naphtholsulphonic acid, 1 : 4, for Pyrotin RRO. Several new dyes were brought out of this Dahl's acid: beta-Naphtol gave a red; naphthol-disulphonic acid, "G", 2 : 6 : 8, gave an orange; its isomeric modification "R", 2 : 3 : 6, gave a red; and then the Schœllkopf's, 1 : 4 : 8, gave the red which was the most resistant. This again pointed to the Schœllkopf's acid, as the most satisfactory to use, if fastness to light was desired. The compound produced by the Dahl's and Schœllkopf's had the proved constitution, $C_{10}H_6(SO_3Na)N=N-C_{10}H_4(SO_3Na)_2.OH$. A sample numbered No. $3\frac{1}{2}$ is annexed.

The writer took up next Naphthionic acid. And it gave some new derivatives, but again the Schœllkopf's acid was the best color from the standpoint of the solidity to the action of the sunlight. The sample of Naphthionic and Schœllkopf is numbered No. 4.

All this seemed to indicate that the Schœllkopf's acid had some very strong staying powers against light, and the Schœllkopf acid itself next became the object of investigation.

The Schœllkopf's acid has already been used for several dyes, patented by the Schœllkopf Aniline and Chemical Co., of Buffalo, N. Y. They are *Wool-Scarlet R*, where diazotized xyldine is used with the Schœllkopf's acid; *Buffalo Rubin*, in which alpha-naphthylamine is applied; *Croceine B*, which is made from diazotized amido-benzene; and *Crocein 3B*, where amido-azo-toluol is utilized.

The experiments which had been made seemed to lead directly to the inference that when any naphthylamine-sulphonic acid was used with the Schœllkopf acid, a dye would result which would be fast to every common reagent. All the obtainable naphthylamine sulphonic acids were tried, and the results are appended. The weights used and the method is given here; the statement is for all the naphthylamine-sulphonic acids. Any naphthylamine-sulphonic acid, of the general formula, $C_{10}H_6.NH_2.SO_3H$, was taken, and 23.2 kilos. were weighed, dissolved in water, and diazotized with 7 kilos. of sodic nitrite and 12 kilos. of hydrochloric acid of twenty Baumé; then 25.4 kilos. of the Schœllkopf's acid, which had been previously

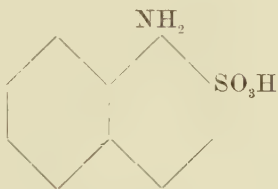
dissolved in water rendered alkaline by the addition of enough sodic hydrate to effect a solution, was added when the dye was immediately formed. The reaction could be facilitated by stirring, and by warming the solution to about eighty degrees C. The dye was salted out in the usual manner, filtered, pressed, dried, and analysed. All the dyes have the same elementary composition, and analysis gives the formula—



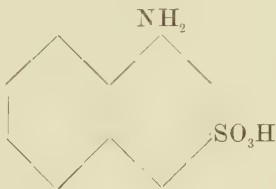
The dyes are reddish powders, readily soluble in water. Hydrochloric acid, even concentrated, produces no perceptible change in the color on the fibre; concentrated sulphuric acid on the dry powder shows a change to a pink of an eosine shade; the dyes are insoluble, as a rule, in alcohol, and are exceedingly fast to the action of sunlight.

The naphtylamine sulphonic acids which can be used are—

Alpha-Naphtylamine-sulphonic acid, 1 : 2, patent No. 56,563,



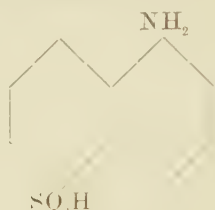
Cleve's alpha-Naphtylamine-sulphonic acid, 1 : 3,



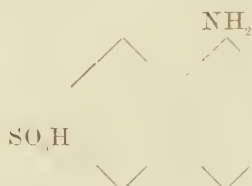
Naphthionic acid, 1 : 4,



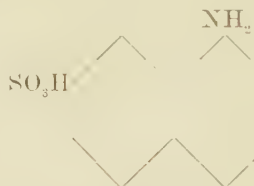
Alpha-Naphtylamine-sulphonic acid, 1 : 5,



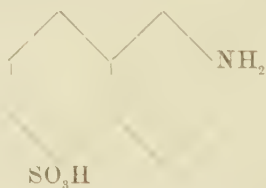
Alpha-Naphtylamine-sulphonic acid, 1 : 6. Bul. Soc. Chim. 26; 447,



Alpha-Naphtylamine-sulphonic acid, 1 : 7. Ber. xxi, 3264,



Beta-Naphtylamine-sulphonic acid, 2 : 5, the so-called Dahl's acid,



Beta-Naphtylamine-sulphonic acid, 2 : 6, the so-called Bronner's acid,



The compound which appeals most strongly to the practical colorist was the derivative obtained when Brønner's and the Schœllkopf acid were joined. This dye was a red which had very remarkable powers of sustaining the prolonged action of the acids used in bleacheries; this gives the dye a commercial value which is not small; further, the dye was very resistant when exposed to the sunlight.

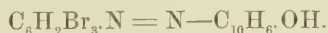
Action of Bromine on the Dyes of the Azo Group.

VI. This group of experiments was carried out with the desire of proving whether the presence of bromine in the dyes of the Azo Group was detrimental or not. The halogens are essential in the production of certain colors, namely, bromine in the production of Eosine from Fluoresceine, and Phloxine from di-chlor-fluoresceine; iodine in changing Fluoresceine to Erythrosine; and the di-chlor-fluoresceine to Rose Bengale. In general the results of the trials seem to indicate that bromine alters the color to the orange side of the red, and gives, as a rule, an undesirable hue.

The writer here wishes to express his sense of the many obligations he is under to Professor C. Loring Jackson, without whose encouragement and counsel the experiments would not have reached a successful termination.

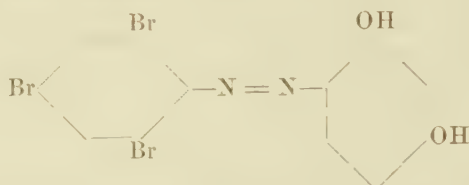
The experiments resolved themselves into the making of a series of chemically pure dyes, and then constructing analogous dyes, which carried bromine in the molecule.

The first dye manufactured was Sudan I, and the corresponding dye which was made with bromine was,



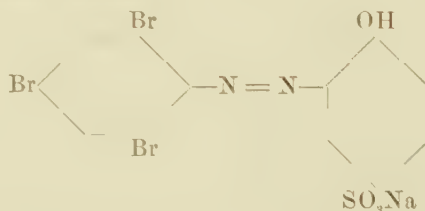
The two colors have the same formulæ, with the exception that one holds the three atoms of bromine. The dyes are readily made; in the case of the Sudan I, aniline is diazotized in the usual manner with sodic nitrite in an acid solution, and coupled with naphthol. For the bromated compound, tri-brom-aniline was made by drawing vapors of bromine through an acidulated solution of aniline hydrochloride, and the precipitated tri-brom-aniline was filtered off, washed, and dried. After diazotization, it was coupled with naphthol, and the dye immediately resulted. The colors are red and orange-red.

When resorcine was utilized, dyes were made of the formulæ,
 $\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})_2$ and $\text{C}_6\text{H}_2\text{Br}_3\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})_2$,
 or written to show graphic constitution,



Another proof was furnished by these two dyes that the bromine was a detriment to clear colors, for the dye with the bromine in its make-up was thrown towards the orange hue again.

Another derivative which would show the difference between dyes holding bromine and those with no bromine in the constitution was the color made when diazotized aniline or tri-brom-aniline respectively, were treated with Neville and Winther's acid, alpha-naphtol-mono-sulphonic acid, 1 : 4. The bromine-holding dye gave the constitutional formula,



The commercial name of the dye without bromine is Tropäolin.

Dyes with the hydroxyl in the beta position were made with and also without bromine. These are the analogue of Crocein Orange or Ponceau 4GB. The formula of the bromated compound is,

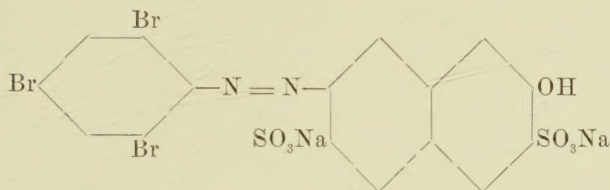


Further details do not seem to be requisite. The comparison of the two dyes, when purified and dyed on wool, show that the bromine flattens the shade.

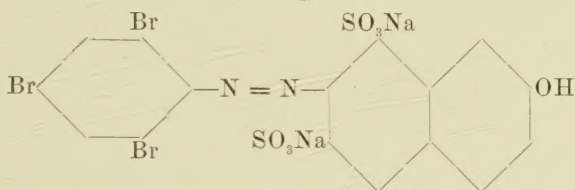
The isomeric beta-Naphtol-di-sulphonic acids, "R" and "G", were the next naphtol sulphonic acids which were utilized with the wish of giving another proof of the possibilities of bromine in the

molecule. The bromine-holding dyes had the following constitution:—

“R”



“G”



The dyes, when compared with their commercial relatives, Ponteau 2G and Orange G extra, have distinctly more orange hues.

Many other dyes were made, but it is deemed unnecessary to multiply instances. Some of this additional work may be mentioned however; when the diazotized tri-brom-aniline was linked with alpha-naphtol a brown-red was made; alpha-naphtylamine gave a red; beta-naphtylamine a brick-red; Bronner's gave a black-red; Dahl's a crimson; tri-sulphonic acid of naphtol a bright red, very soluble in water.

SCHOOL OF MINES, COLUMBIA COLLEGE, March 15, 1894.

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in Chemistry ;
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Mulhouse (Alsace), Farbe-Schule (Prof. Nœlting), two terms ;
Weber's Works, Switzerland, as Voluntär, $\frac{1}{2}$ year ;
Practical Work, Norwich, Ct., and Providence, R. I., 1888-1891 ;
Graduate Student, Harvard University, 1891-1893 ;
University Assistant, and Private Assistant, Harvard, 1891-1893 ;
University Fellow in Chemistry, Columbia College, 1893-1895.